

OFFICE OF NAVAL RESEARCH  
END-OF-THE-YEAR REPORT  
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT  
for  
GRANTS: N00014-94-1-0704 and N00014-98-1-0155  
PR Numbers: 98PR03148-00 & 98PR02359-00

*Very Low Surface Energy ( $<11 \text{ dyn cm}^{-1}$ ) Heterophase Polymeric Materials for  
Membrane Separations: An Integrated Polymer Chemistry/Engineering Approach*  
and

*The Influence of Backpulsing on Fouling Properties of  
Novel Nanofiltration Membranes for Wastewater Remediation*

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Submitted: July 13, 1998

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OFFICE OF NAVAL RESEARCH

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

PR Number: 98PR03148-00 & 98PR02359-00

Contract/Grant Number: N00014-94-1-0704 & N00014-98-1-0155

Contract/Grant Title: Very Low Surface Energy ( $< 11 \text{ dyn cm}^{-1}$ ) Heterophase

Polymeric Materials for Membrane Separations: An Integrated Polymer

Chemistry/ Engineering Approach & The Influence of Backpulsing on Fouling

Properties of Novel Nanofiltration Membranes for Wastewater Remediation

Principal Investigators: Professors Benny D. Freeman [both grants] and Joseph M.

DeSimone [grant N00014-94-1-0704 only]

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http addresses: <http://che.ncsu.edu/membrane> (Freeman),

<http://net.chem.unc.edu/faculty/jmd/jmdhmpg.html> (Desimone)

a. Number of papers submitted to refereed journals, but not published: 2

Arnold, Nagai, *et al.*, "Gas Permeation Properties of Fluorinated Polymers: PFOA, PFOMA, and PS-b-PFOA Copolymers," manuscript in preparation.

Arnold, Betts, LeRoux, *et al.*, "Synthesis and Characterization of PDMAEMA-b-PFOMA Copolymers," manuscript in preparation.

b. Number of papers published in refereed journals: 0

c. Number of books or chapters submitted, but not yet published: 0

d. Number of books or chapters published: 3

Betts, Douglas E., "The Synthesis, Characterization, and Application of CO<sub>2</sub>-Soluble, Nonionic Amphiphilic Block Copolymers," Doctoral Dissertation, Department of Chemistry, University of North Carolina at Chapel Hill, 1998.

Kassis, Camille Mary, "Surface and Mass Spectral Analysis of Polymeric Materials Utilizing X-ray Photoelectron Spectroscopy and Matrix Assisted Laser Desorption Ionization," Doctoral Dissertation, Department of Chemistry, University of North Carolina at Chapel Hill, 1997.

Betts, D.E., Johnson, T., LeRoux, D., DeSimone, J.M., "The Use of Controlled Radical Polymerization Methods for the Synthesis of Non-ionic Surfactants for CO<sub>2</sub>," in Controlled Radical Polymerization; Matyjaszewski, K., Ed., ACS Symposium Series 685, American Chemical Society: Washington, DC, 1998, pp. 418-432.

e. Number of printed technical reports/non-refereed papers: 0

f. Number of patents filed: 0

g. Number of patents granted: 0

h. Number of invited presentations: 3

Freeman, B.D., M.E. Arnold, and K. Nagai, "Development of Novel, Low-Fouling Nanofiltration Membrane Materials: Program Overview," Office of Naval Research, June 3, 1998, Jacksonville, FL.

Johnson, T., J.M. DeSimone, and D. Betts, "Fluoropolymer Block Copolymer Synthesis for Membrane Applications," Office of Naval Research, June 3, 1998, Jacksonville, FL.

Pinnau, I. (MTR), R. Bhave (U.S. Filter), and B. Freeman (NCSU), Membrane Materials Workshop, North American Membrane Society Meeting, May 1998, Cleveland, OH.

i. Number of submitted presentations: 3

Nagai, K., M. Arnold, R.J. Spontak, B.D. Freeman, D. LeRoux, D. Betts, J.M. DeSimone, A.R. Roudman, F.A. DiGiano, and I. Pinnau, "Pure Water and Salt Permeation Properties of Phase-separated Block Copolymers of Poly(1,1'-dihydroperfluorooctylalkyl-methacrylate-*b*-2-dimethylaminoethyl methacrylate)", North American Membrane Society Meeting, May 1998, Cleveland, OH.

Allen, T., B.D. Freeman, D.T. Coker, and G.K. Fleming, "Modeling Temperature Distributions in Multicomponent Membrane Separations," North American Membrane Society Meeting, May 1998, Cleveland, OH.

Arnold, M., K. Nagai, B.D. Freeman, D. Betts, J. DeSimone, and I. Pinnau, "Gas Permeability in Fluorinated Block Copolymers," North American Membrane Society Meeting, June 4, 1997, Baltimore, MD.

j. Honors/Awards/Prizes for contract/grant employees: 5

Freeman, B.D., Nominated for Alumni Association Distinguished Undergraduate Professor, 1998

Betts, D., awarded Ph.D., Department of Chemistry, University of Chapel Hill, 1998.

Burns, S., passed preliminary oral examination required for official candidacy in Ph.D. program, Department of Chemistry, University of Chapel Hill.

Freeman, B.D., Japan Society for the Promotion of Science Fellowship, 1997.

Kassis, C.M., awarded Ph.D., Department of Chemistry, University of Chapel Hill, 1997.

k. Total Number of Full-time equivalent Graduate Students and Post-Doctoral associates supported during this period, under this R&T project number: 4

Graduate Students: 3 1/12

Post-doctoral Associates: 11/12

including the number of,

Female Graduate Students: 2 11/12

Female Post-Doctoral Associates: 0

the number of

Minority\* Graduate Students: 2

Minority\* Post-Doctoral Associates: 0

and, the number of

Asian Graduate Students: 1/6

Asian Post-Doctoral Associates: 1

l. Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant)

Department of Defense SERDP Program, "Novel Nonporous Fouling-Resistant Composite Nanofiltration Membranes and Membrane Separation Systems for Wastewater Treatment Important for CPSON5/PPSON1: Minimization of Oily and Non-Oily Waste," \$0, \$1,402,106, 6/4/98-5/14/2001. This grant provides funding for a collaborative research project between Dr. Freeman's research group at North Carolina State University and Membrane Technology and Research, Inc. [MTR]. This academic/industrial partnership is directed towards removing fundamental

wastewater processing limitations related to membrane fouling by developing advanced high flux, low fouling membrane materials and reducing these advances to practice by preparing spiral wound membrane units suitable for field testing.

NSF, "Gel Permeation Chromatograph for Polymers and Colloid Science Research Program," \$56,666.67, \$85,000, 10/97-9/98. This NSF equipment grant provides funds for purchasing a state-of-the-art gel permeation chromatograph for use in determining molecular weights, molecular weight distributions, and composition distributions in polymers. This instrument will assist in characterization of the novel materials being synthesized for the ONR program.

American Water Works Association, "Development and Testing of New Nanofiltration Membranes for Application to Water Treatment," \$18,000, \$18,000, 10/97-10/99. This grant is for studying low-fouling membranes for purification of drinking water and complements the Navy research program which is vectored towards wastewater remediation.

Office of Naval Research, " Characterization of Ultra-Low Fouling Reverse Osmosis and Pervaporation Membranes for Naval Wastewater Remediation Applications," \$36,902, \$107,521, 6/1/95-5/31/98. This AASERT grant provides additional personnel to work directly on the Navy program.

- a. Principal Investigators: Benny D. Freeman and Joseph M. DeSimone
- b. Current Telephone Number: (919)515-2460 (Freeman) and (919)962-2166 (DeSimone)
- c. Cognizant ONR Program Officer: Kenneth J. Wynne
- d. Program Objectives

The focus of our fundamental research program, *Very Low Surface Energy (<11 dyn cm<sup>-1</sup>) Heterophase Polymeric Materials for Membrane Separations: An Integrated Polymer Chemistry/Engineering Approach*, is to explore several new classes of polymeric materials to identify promising routes for developing low-fouling nanofiltration membranes for wastewater remediation. This objective will be accomplished through an iterative process of polymer synthesis and characterization, membrane fabrication, separation performance characterization, and fouling assessment. Three classes of materials are being evaluated: low surface energy heterophase fluoropolymeric materials (synthesized by DeSimone's group), functionalized nanoporous polymeric membranes with well-defined pore size formed via lyotropic liquid crystalline monomers (in collaboration with Professor Douglas L. Gin at the University of California at Berkeley), and nonporous hydrophilic blend membrane materials (in collaboration with Professor Virgil Percec at Case Western Reserve University). The focus of our closely related research program, *The Influence of Backpulsing on Fouling Properties of Novel Nanofiltration Membranes for Wastewater Remediation*, is to determine the efficacy of backpulsing to reduce the fouling of nanofiltration membranes.

- e. Significant results during last year

Substantial progress has been made towards developing membrane materials suitable for wastewater remediation. In addition to more fully characterizing the PDMAEMA-b-PFOMA\* (containing 52, 55, 67, and 69 mol% PDMAEMA) copolymers synthesized last year, PTAN-b-PDMAEMA (69 mol%)-b-PDMAEMA and PFOMA-b-PDMAEMA (59 mol%)-b-PFOMA triblock copolymers have been synthesized and characterized using angle-dependent x-ray photoelectron spectroscopy (ADXPS), water sorption, salt transport, and water permeation measurements. Dense films of the polymers were cast from 10 (w/v) % polymer dissolved in Freon-113 with the

exception of the PTAN\* triblock films which were cast using  $\alpha, \alpha, \alpha$ -trifluorotoluene as the solvent.

Water uptake and water flux increase with increasing PDMAEMA (hydrophilic block) content of the copolymer and are well correlated. The PTAN triblock copolymer has the highest water uptake and water permeability, suggesting that fluoropolymer morphology also influences water sorption and permeation. PTAN is a fluorinated acrylate whose side chains can crystallize, while PFOMA is a fluorinated methacrylate whose side chains cannot crystallize. No strong correlation is found between salt diffusivity or distribution coefficient with either PDMAEMA content or water uptake. Therefore, differential scanning calorimetry (DSC) was used to determine the amounts of freezing and non-freezing water present in these materials. For PFOMA-based materials, the amount of non-freezing water (which is tightly bound to the hydrophilic groups) decreases as the PDMAEMA (or hydrophilic) content increases. The PTAN triblock copolymer does not appear to follow the same trends as the PFOMA-based materials and also possesses the highest number of non-freezing water molecules per hydrophilic group among the materials tested to date. The salt diffusion coefficient increases with the fraction of freezing water sorbed by the polymer (as shown in the figure in Part III); these data suggest that only freezing water (or water which is not tightly bound to hydrophilic groups) is available for salt diffusion. The free volume theory developed by Yasuda and co-workers to explain the transport of small molecules in water-swollen polymeric membranes cannot be used to explain the salt diffusion results until hydration is corrected to include only the regions of freezing water present within the hydrophilic regions of the polymers. Then the sodium chloride diffusion coefficient for the PFOMA-based materials is inversely related to hydration, in agreement with the free volume theory. The PTAN triblock copolymer results are not well-correlated with the other data points, again implying that morphological factors influence diffusion. Salt distribution coefficients are less than the hydration values for these polymers, suggesting that polymer-salt interactions affect the overall salt solubility. ADXPS results for the PTAN-PDMAEMA (69 mol%)-b-PTAN sample indicate that the copolymer is surface segregated. Even after annealing the samples far above their glass transition



temperatures, there was no change in angle-dependent atomic concentrations or fluorinated carbon to total carbon ratios. These results suggest that the triblock architecture restricts reorganization of the copolymer chains. Moreover, the theoretical fluorine-to-carbon ratio of pure PTAN is 2.1, and the experimental ADXPS ratios of both the unannealed and annealed sample are 2.0, which indicates that the near-surface region is comprised mostly of PTAN.

Functionalized nanoporous polymeric films containing sodium, cobalt (II), and cadmium (II) ions were received from Professor Douglas Gin and Dr. Hai Deng. Water uptake was investigated as a function of film thickness (*ca.* 25, 50, and 100  $\mu\text{m}$  films) for liquid crystalline polymeric samples, and these sorption results are shown in the attached figure. Water uptake increases with increasing film thickness for sodium and cobalt (II) samples, while water sorption in cadmium (II) films is independent of film thickness. While all materials studied sorbed measurable quantities of water, no measurable water permeation was observed for any sample, implying that the channels are not continuous and open across the sample.

Samples of Trogamide T/Poly(vinyl pyrrolidone) (TA/PVP), Poly(methacrylic acid)/Poly(vinyl pyrrolidone) (PMAA/PVP), and Trogamide T/Poly(2-ethyl-2-oxazoline) (TA/PEOXA) blends received from Dr. Tushar Kanti Bera and Professor Virgil Percec were too small to perform water permeation measurements. However, based upon the flexibility of these materials in the dry/wet states and the supplied water sorption data, only the TA/PEOXA and TA/PVP blend series were chosen for scale-up and further characterization. The attached figure shows the water sorption and glass transition behavior of these materials as a function of blend composition.

\*PDMAEMA = poly(diethylaminomethacrylate), PFOMA = poly(1,1-dihydroperfluoro-octylmethacrylate), PTAN= 3D poly telomer acrylate with narrow distribution

f. Brief summary of plans for next year's work

In the next year, research efforts will continue to focus on developing and characterizing a systematic series of nonporous hydrophilic block copolymers for nanofiltration wastewater remediation applications. Recently acquired TEM results for the PDMAEMA family of block

copolymers will be used to understand the relationship between morphological structure and transport properties for this class of materials. Finally, a series of PTAN-b-PDMAEMA copolymers of varying composition as well as PTAN-b-PDMAEMA-b-PTAN and PDMAEMA-b-PFOMA copolymers of additional compositions will be synthesized and characterized. Hydrophilic block copolymers containing hydroxy ethyl acrylate (HEA) as the hydrophilic block will be investigated. TEM and ADXPS will continue to be used as characterization methods for these new materials. Water permeability, salt diffusivity, and salt distribution coefficients will be measured for the new materials.

Additional crossflow experiments will be performed using PDMAEMA-b-PFOMA thin-film composite membranes (containing 55 and 69 mol% PDMAEMA) to determine model contaminant rejection and fouling properties of these materials. Methods to prepare thin-film composite membrane samples at NCSU will also be investigated. Finally, copolymer samples will be sent to Dr. Harry Ridgway at the Orange County Water District (OCWD) for biofouling and atomic force microscopy (AFM) [used to measure surface roughness] characterization.

Research efforts by Professor Douglas Gin's group will be focused towards modifying membrane properties to achieve water permeation through these functionalized nanoporous materials. Approaches used will include: altering the water content in the films to increase the pore size and/or render the films less hydrophobic, aligning channels to ensure continuous pores through polymerizing in magnetic fields, and utilizing plasma etching to verify that pores are not closed at the surface. The water sorption and permeation properties of new samples will be determined at NCSU.

TA/PVP and TA/PEOXA blend samples of systematically varied composition have recently been supplied in larger (4.5 - 5 g) quantities. Water permeation will be measured using films of uniform thickness.

A backpulsing unit, capable of controlling pressure difference across a membrane to  $\pm 2$  psi, was custom-built by Separations System Technology, Inc. (San Diego, CA). In the next year, experiments will be conducted to explore the effects of backpulse time, pressure, fluid volume, and

frequency on the average flux of a series of commercially available membranes (for benchmarking purposes) as well as materials synthesized for ONR grant N00014-94-1-0704.

g. List of names of graduate students and post-doctoral fellows currently working on the project:

Michelle Arnold (NCSU)

Dr. Valeriy Bondar (NCSU)

Dr. Kazukiyo Nagai (NCSU)

Sonya Burns (UNC)

Terri Johnson (UNC)

# Heterophase Polymeric Materials for Membrane Separations

Freeman, North Carolina State University; DeSimone, University of North Carolina at Chapel Hill

**Technology Issues:** Nanofiltration membrane materials must be low-fouling, permeable, and selective

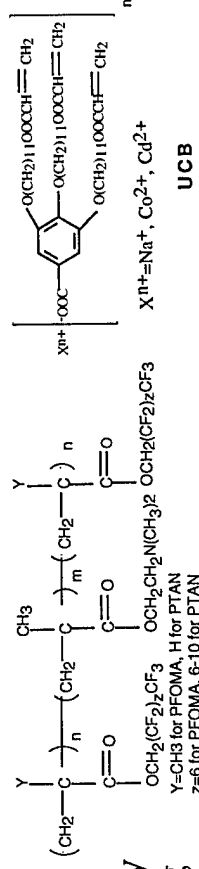
**Objectives:** Develop novel heterophase membrane materials for wastewater remediation; Determine efficacy of backpulsing to reduce nanofiltration membrane fouling

## Approach:

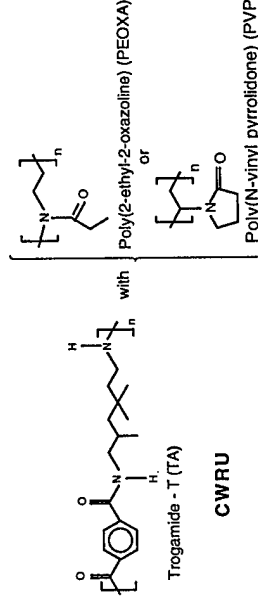
- Synthesize and characterize properties (structure, morphology, permeation, rejection, and fouling) of several classes of polymeric materials:
  - Low surface energy heterophase fluoropolymeric materials (with J.M. DeSimone, UNC)
  - Uniform pore size liquid crystalline membranes (with D. Gin, UCB)
  - Nonporous hydrophilic polymer blends (with V. Percec, CWRU)
- Investigate effects of backpulse time, pressure, fluid volume, and frequency on average flux

## Accomplishments:

- Diblock & triblock copolymers of PDMAEMA (hydrophilic block) and PTAN/PFOMA (low surface energy block) have been synthesized and characterized (with UNC)
  - Materials have high water sorption and water flux levels; sorption and flux are highly correlated
- Liquid crystalline membranes functionalized with  $\text{Na}^+$ ,  $\text{Cd}^{2+}$ , and  $\text{Co}^{2+}$  ions have been characterized (with UCB)
  - Materials have measurable water uptake but no measurable water permeation, suggesting the need to open channels
- Nonporous hydrophilic polymer blends have been selected for scale-up and further characterization (with CWRU)
  - A backpulsing crossflow membrane unit has been designed and built



UNC

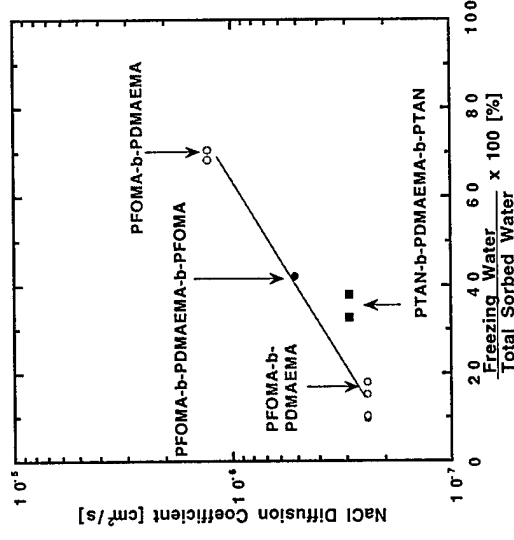
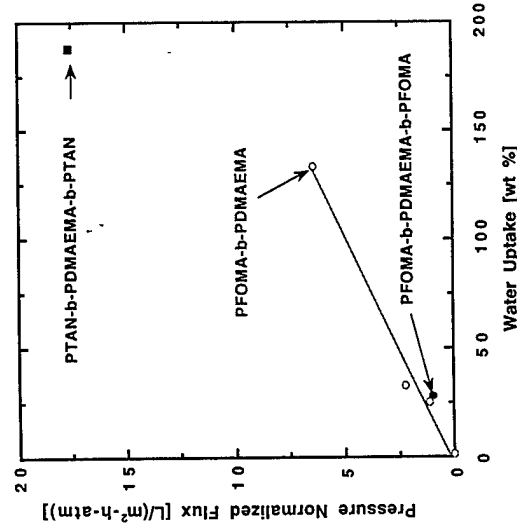


CWRU

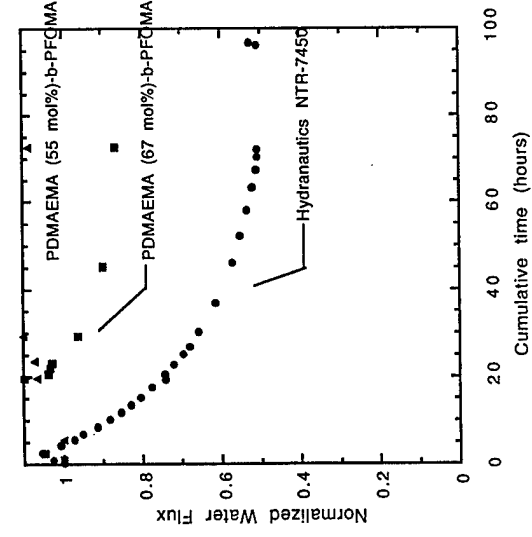
## Transitions:

- Rejection and fouling properties of fluoropolymeric materials will be studied (with UNC)
- Copolymers with different hydrophilic blocks (e.g., HEA) will be synthesized and characterized
- Plasma milling will be used to open channels of liquid crystalline materials (with UCB)
- Water permeation properties of hydrophilic polymer blends will be investigated (with CWRU)
- Backpulsing experiments will be begun

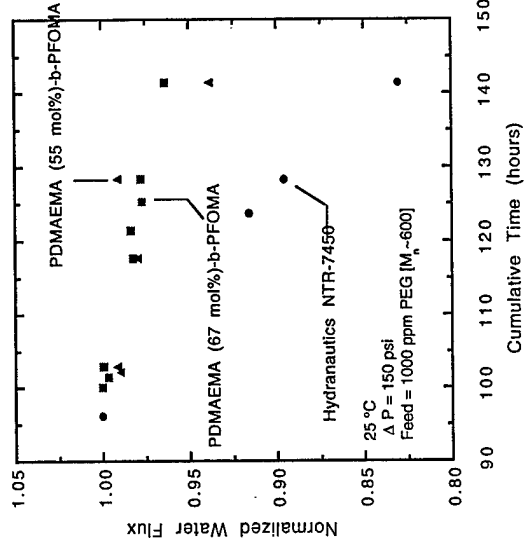
# Characterization of UNC copolymers



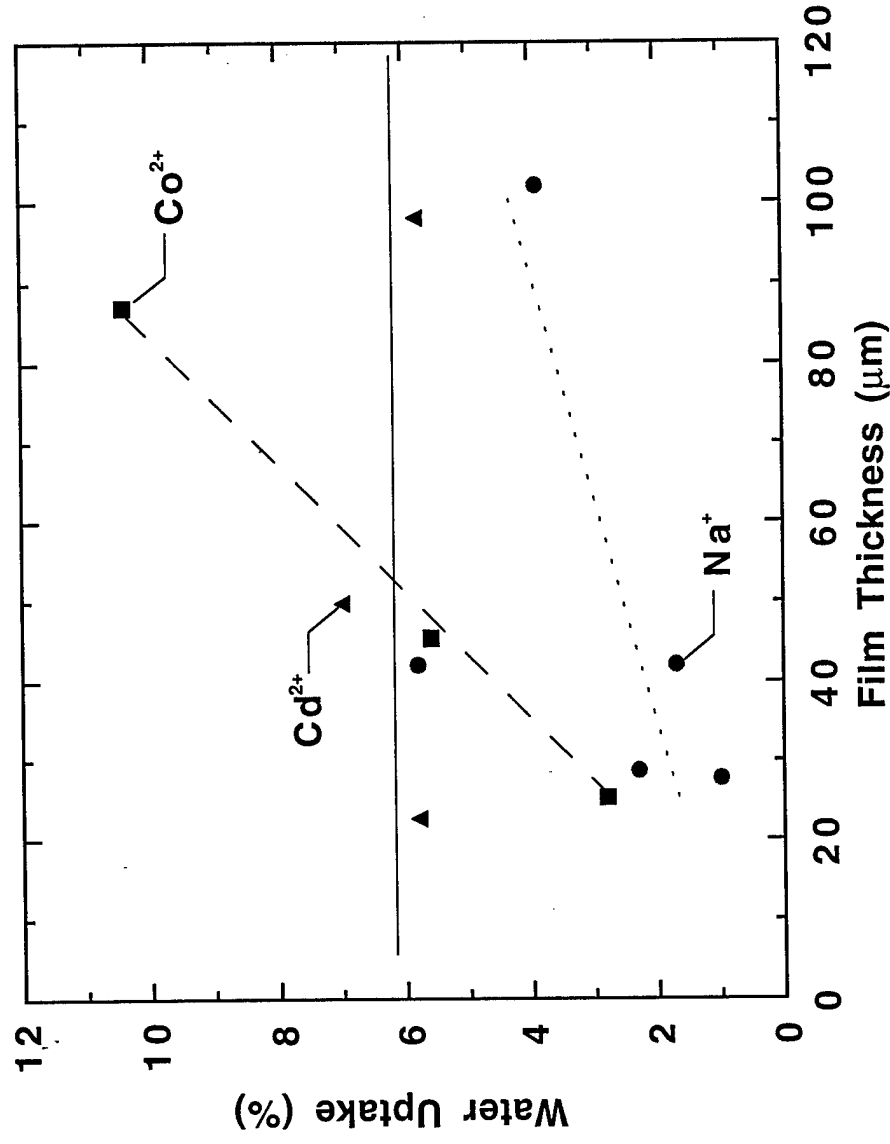
Water flux during initial setting period



Water flux upon exposure to PEG



# Water Uptake of UC Berkeley Samples

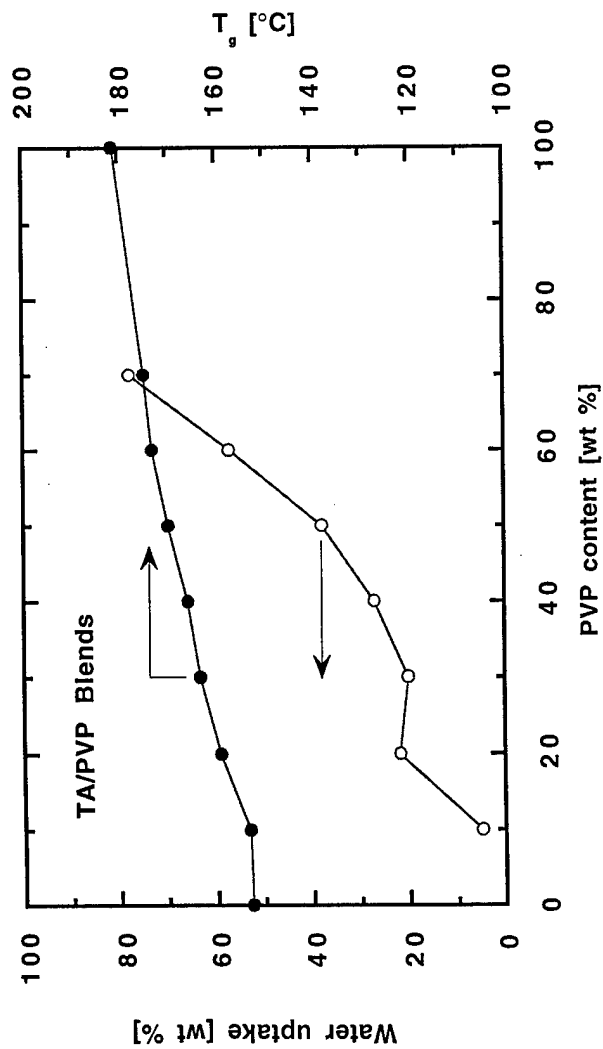
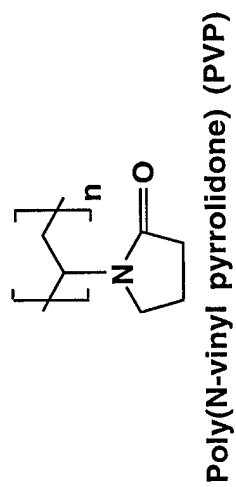
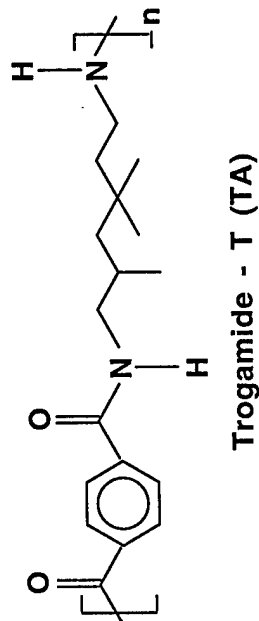
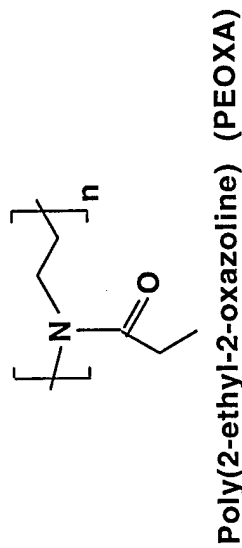
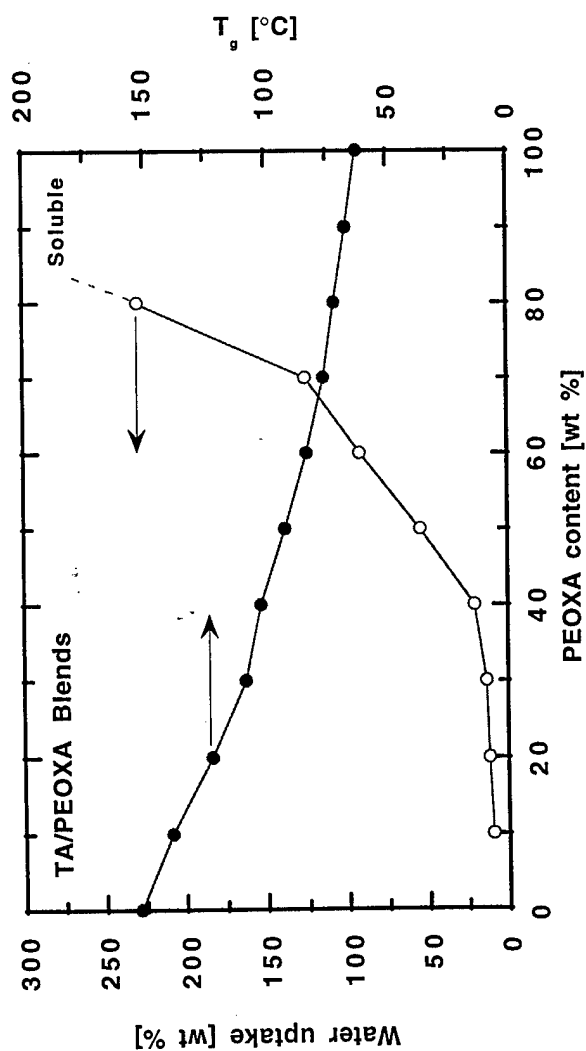


Measurable water uptake is observed for all samples.

Water uptake depends on thickness for cobalt and sodium-based materials.

No measurable water permeation was observed for any sample, suggesting that channels are not continuous or open across the sample.

# Nonporous Hydrophilic Blends (with CWRU)



The introductory viewgraph presents an overview of our research efforts to develop heterophase polymeric membrane materials for wastewater remediation. Nanofiltration materials must be low-fouling, permeable, and selective. Since it is difficult to achieve all of these properties in a single material, several classes of heterogeneous materials are being synthesized and characterized with respect to structure, morphology, permeation, rejection, and fouling: low surface energy fluoropolymer materials with Professor DeSimone at UNC, uniform pore size liquid crystalline materials with Professor Gin at UCB, and nonporous hydrophilic blends with Professor Percec at CWRU. The visual shows representative chemical structures for each class of materials. The UNC materials investigated to date are diblocks or triblocks consisting of PDMAEMA hydrophilic blocks and PFOMA or PTAN low surface energy blocks. The UCB monomer which is photopolymerized to yield films with uniform pore size is shown to the right of the UNC structures. The CWRU samples which are being scaled up consist of either a hydrophilic poly(2-ethyl-2-oxazoline) [PEOXA] or poly(N-vinyl pyrrolidone) [PVP] component blended with Trogamide-T. Progress has been made in characterizing each type of material. Diblock and triblock copolymers of PDMAEMA with PFOMA or PTAN have been synthesized and their fundamental transport properties (water uptake, water permeation, salt diffusivity, and salt partitioning) have been characterized. In the next year, the fouling and rejection properties of these materials will be studied. Additionally, copolymers with a different hydrophilic block, such as hydroxy ethyl acrylate [HEA], will be synthesized and characterized. In collaboration with UCB, liquid crystalline membranes functionalized with  $\text{Na}^+$ ,  $\text{Co}^{2+}$ , and  $\text{Cd}^{2+}$  ions have been prepared and characterized for water sorption and permeation properties. The next step is to use plasma milling to open the channels of these materials. Based upon



mechanical data (*i.e.*, whether the films are flexible or brittle), water sorption and glass transition temperature data, several nonporous hydrophilic blends were selected for scale-up and further characterization. The water permeation properties of these materials will be investigated as a function of blend composition. Finally, this viewgraph presents the objective of our closely related research program to determine the efficacy of backpulsing to reduce nanofiltration membrane fouling. The effects of backpulse time, pressure, fluid volume, and frequency on the average flux of the commercially available standards as well as materials synthesized for ONR grant N00014-94-1-0704 will be investigated. As the initial step, a backpulsing crossflow membrane unit has been designed and built by Separation Systems Technology, Inc. Backpulsing experiments will be begun this year.

The second slide shows selected characterization results for the low surface energy fluoropolymeric materials from UNC. The first graph illustrates the close correlation between pressure-normalized flux and water uptake for these materials. Generally, as the hydrophilic content of the copolymer increases, both water flux and sorption increase. The PTAN triblock has the highest water flux and sorption level. Since the PTAN side chains can crystallize, this phenomenon may be due to crystallization-assisted hydrophilic domain alignment. The transport data will be analyzed in terms of morphological structure of the samples in the coming year. The second graph shows the sodium chloride diffusion coefficient as a function of the freezing water content of the material. The diffusion coefficients for the PFOMA-based materials are well correlated with a free volume model when the hydration is corrected to include only the freezing water content. The diffusion coefficient for the PTAN triblock lies below the correlation for the PFOMA-based materials, suggesting that morphological effects influence salt diffusivity. The third and fourth plots show water flux versus time both for the initial setting period and in the presence of polyethylene glycol [PEG with  $M_n \sim 600$ ]. Both PDMAEMA(67 mol%)-b-PFOMA and PDMAEMA(55 mol%)-b-PFOMA thin-film composite membranes showed less flux decline in this

run than the commercial control Hydranautics NTR-7450 (sulfonated polyethersulfone) nanofiltration membrane.

The third slide presents water uptake of the UCB samples as a function of film thickness for  $\text{Na}^+$ ,  $\text{Co}^{2+}$ , and  $\text{Cd}^{2+}$  functionalized materials. Water uptake is measurable for all samples, and it appears to depend on film thickness of the  $\text{Co}^{2+}$  and  $\text{Na}^+$  materials. However, no measurable water permeation was observed for any sample, implying that the channels are not continuous throughout the samples. Plasma milling will be used to open these channels.

The fourth slide presents water uptake and glass transition data as a function of the hydrophilic blend component of the CWRU materials. For the TA/PEOXA and TA/PVP blends, water uptake, increases as the hydrophilic (*i.e.*, PEOXA or PVP) content is increased. Both series show a single  $T_g$  for each blend composition, indicating that these materials are not phase-separated. The glass transition temperatures of the TA/PEOXA series decrease as the PEOXA content increases, while the  $T_g$  of the TA/PVP series increases as the PVP content increases. These materials are being scaled up to larger sample quantities, and their water permeation properties as a function of blend composition will be investigated this year.